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Electron trap liberation in MgF_2 doped with Yb^{2+} using a two-color excitation experiment

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We utilize the optical transitions of Yb^{2+} excited by an ultraviolet optical parametric amplifier to probe electron trap liberation in MgF_2 via the observation of a photoluminescence enhancement effect induced by a subsequent infrared pulse from a free-electron laser. The temperature dependence of the enhancement suggests that we liberate very shallow traps having a depth of approximately 17 cm^{-1} . The observed "trap spectrum" is consistent with a simple model of a Coulomb trap. © 2012 American Institute of Physics. [doi:10.1063/1.3678630]

The interconfigurational $f \rightarrow d$ transitions of both trivalent and divalent lanthanide ions have attracted extensive interest over recent years as increasing availability of high energy light sources have made comprehensive investigations of the energy-level structure of the excited configuration more readily practicable.¹ These investigations are most often driven by possible applications in tunable ultraviolet (UV) lasers or efficient mercury-free lighting.

A complicating feature of the emission spectra obtained from some lanthanide-doped materials is the presence of impurity-trapped excitons (ITE) which form the lowest-energy emitting state under certain conditions.² The ITE consists of a hole localized on the lanthanide ion and an electron delocalized on the neighboring metal cations. The ITE emission is typified by a significant red shift and broadening relative to the absorption, as well as long (up to tens of milliseconds) lifetimes. ITE emission (often termed "anomalous" emission) is most commonly observed for divalent lanthanides (Eu^{2+} and Yb^{2+}).

We have recently demonstrated that it is possible to study in detail the energy level structure of ITE in $\text{CaF}_2:\text{Yb}^{2+}$ using a two-color transient photoluminescence enhancement technique^{3,4} which is similar to that reported earlier.⁵ Our technique uses short-pulsed UV excitation of the interconfigurational $f \rightarrow d$ transitions with subsequent formation of the ITE. The pulsed infrared (IR) output of a free-electron laser (FEL) is spatially overlapped with the UV beam and given a short temporal delay relative to the lifetime of the ITE emitting state(s), i.e., around $100\text{ }\mu\text{s}$. As the FEL wavelength is widely tunable we may scan through any intra-excitonic transitions in a given wavelength region. When the FEL is resonant with an ITE transition an increase in the luminescence intensity is observed at the time delay given to the FEL pulse. This occurs because the first excited

exciton level (at 40 cm^{-1}) has a shorter radiative lifetime than the lowest emitting level. Thus, whenever we populate high-lying exciton states, non-radiative relaxation leads to a significant population in the first excited level yielding an increase in the emission on a timescale associated with the overall lifetime of the first excited state. In those experiments IR enhancement was also observed that decayed with the radiative lifetime of the lowest ITE state. This was interpreted as liberation of electrons from shallow traps that were subsequently captured at the lanthanide sites.⁴

Here we report results for MgF_2 crystals doped with divalent ytterbium. The luminescent properties of $\text{MgF}_2:\text{Yb}^{2+}$ have been reported previously.⁶ In MgF_2 , divalent ytterbium occupies the Mg^{2+} site, which is six-coordinate and has D_{2h} point group symmetry. Characteristic $f \rightarrow d$ absorption and emission appears to have been observed although it has been suggested that this system could exhibit ITE emission.² That the observed emission has its origin in $d \rightarrow f$ transitions is fairly strongly supported by the fact that the red shift between the lowest energy absorption peaks and the emission is small and that vibronic structure is observed. This is most certainly not the case in the Yb^{2+} doped CaF_2 and SrF_2 systems.

The experiments described here employed highly polished crystals cut from the same boule as those used in the earlier study of Lizzo.⁶ They contained 0.6 mol% of ytterbium and were grown using the Bridgman technique in a reducing atmosphere. 335 nm excitation was provided by a Quantronix TOPAS traveling wave optical parametric amplifier (OPA) having a repetition rate of 1 kHz and a pulse length of 3 ps. The Dutch free-electron laser (FELIX) in Nieuwegein was used to excite the samples in the infrared. The output of FELIX consists of a $6\text{ }\mu\text{s}$ long macropulse with a repetition rate of 10 Hz in the experiments performed here. The IR radiation was tuned between 5 and $25\text{ }\mu\text{m}$. The two lasers were synchronized and have an electronically variable delay, which was limited to less than one millisecond due to the repetition rate of the OPA. The two beams were spatially

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overlapped on the sample with a spot size of close to $100\ \mu\text{m}$. The resultant fluorescence was collected using a TRIAX 320 spectrometer and detected with an RCA C31034 photomultiplier tube.

Figure 1(a) shows the 10 K photoluminescence decay of $\text{MgF}_2\text{:Yb}^{2+}$ under UV excitation of the $f \rightarrow d$ inter-configurational transitions at a wavelength of 335 nm, through the direct excitation of the E band of Lizzo.⁶ Emission is monitored at 475 nm, which is the peak of the emission band. This underlying transient is well approximated by a single exponential decay having a decay time of 7.5 ms and is entirely consistent with the findings of Ref. 6. The increase in photoluminescence observed at a time delay of $150\ \mu\text{s}$ arises from the application of an infrared pulse from the FEL. The IR wavelength used was $750\ \text{cm}^{-1}$ ($13.3\ \mu\text{m}$), and no IR pulse was applied in the preceding UV excitation period. It can be seen that the application of the IR pulse induces an increase in the emission detected from the sample of up to 8% and that the enhanced emission component decays with the same characteristic lifetime that is observed in the absence of the IR excitation. This suggests that the enhanced emission arises from the same emitting state and is therefore quite unlike that observed for the ITE emission in $\text{CaF}_2\text{:Yb}^{2+}$ for example. We have also varied the time delay

between the excitation pulses from 40 to $600\ \mu\text{s}$ and have found no variation in the temporal characteristics.

Figure 1(b) shows the temporal evolution of the emission spectrum under the application of both the UV and IR pulses with a shorter time delay of $50\ \mu\text{s}$ between them. There is signal preceding the arrival of the UV pulse at $t = 0$ because the lifetime of the Yb^{2+} emission exceeds the repetition rate of UV laser. What is immediately obvious is that there is no spectral shift observed in the spectrum upon the arrival of the IR pulse. Again, this is in contrast to the spectral behavior of the ITE photoluminescence enhancement (Ref. 3, Fig. 1(b)) where emission from different states with substantially different bond lengths yields considerable spectral shifts under IR excitation and therefore the available population of emitters is shifted around in both the time and spectral domains. Thus it seems reasonable to conclude that the observed emission spectrum from $\text{MgF}_2\text{:Yb}^{2+}$ is indeed $d \rightarrow f$ emission, as suggested in Ref. 6.

We observe that for a given IR fluence the fractional enhancement of the signal does not depend on the UV excitation density up to $14\ \text{GW}/\text{cm}^2$, the maximum available from the UV source. However, the fractional enhancement increases with IR excitation density, and there is clear evidence of the onset of saturation, as is shown in Fig. 2(a).

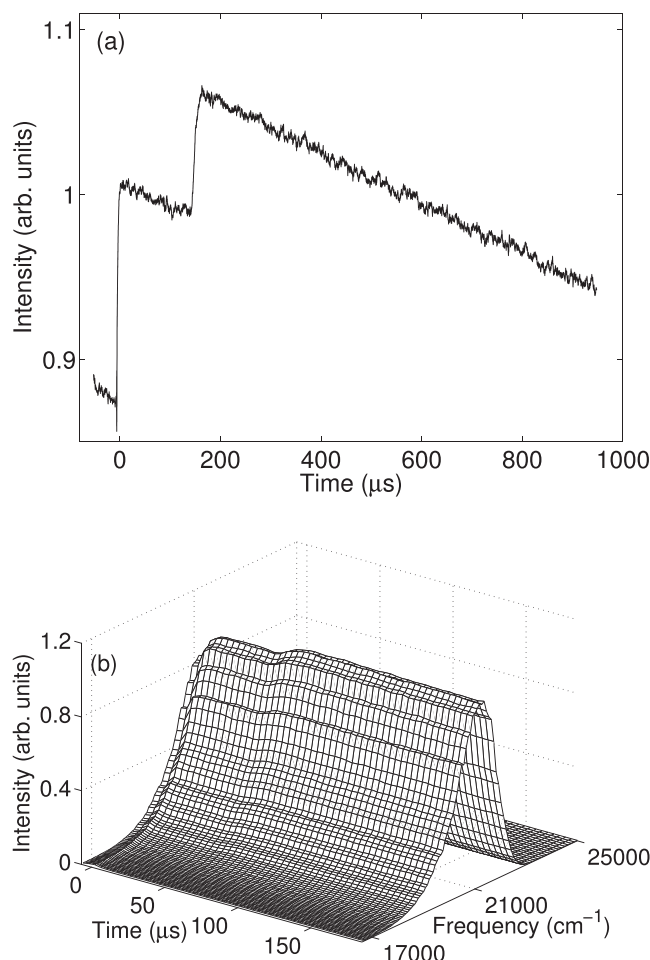


FIG. 1. (a) 10 K photoluminescence decay for $\text{MgF}_2\text{:Yb}^{2+}$ showing enhancement under $150\ \mu\text{s}$ delayed FEL excitation at $13.3\ \mu\text{m}$ and (b) spectrally resolved photoluminescent decay shown on a shorter time scale with the FEL excitation time delayed by $50\ \mu\text{s}$.

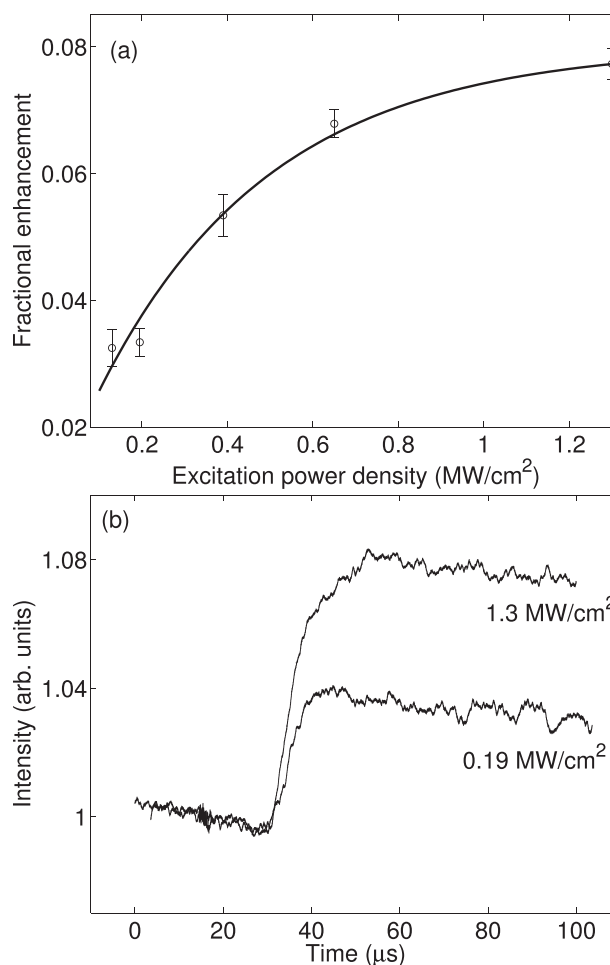


FIG. 2. (a) Fractional magnitude of the enhancement effect as a function of IR power and (b) low- and high-power risetimes on the IR induced enhancement of the Yb^{2+} photoluminescence. The solid line in (a) is a fit to an exponentially saturating process.

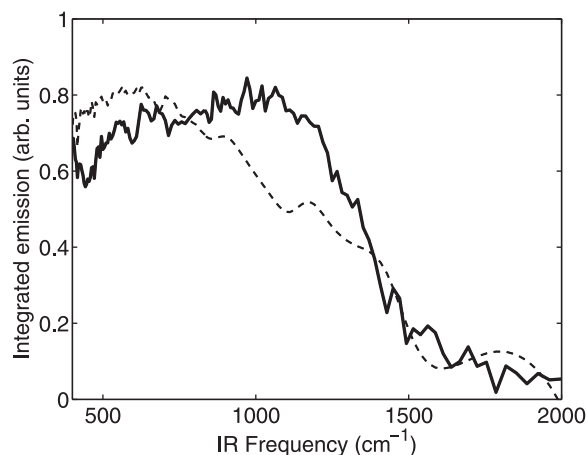


FIG. 3. The solid line is the 10 K trap-liberation spectrum of $\text{MgF}_2\text{:Yb}^{2+}$ and the dashed line is the FEL power curve measured just before the cryostat.

This is accompanied by an increasing rise-time observed on the transient photoluminescence enhancement itself (Fig. 2(b)). The low-power rise-time essentially matches the macropulse length of $6\text{ }\mu\text{s}$, i.e., it is instrument limited. However, at the highest powers we observe rise-times as long as $21\text{ }\mu\text{s}$.

The origin of the photoluminescence enhancement can most likely be attributed to the IR pulse liberating electron traps, which become populated upon application of the UV pulse through photoionization into the conduction band. In effect, the IR pulse at least partially reverses the cycle and the liberated electrons relax back into the Yb^{2+} d shell. Therefore, the IR pulse increases the total available population of emitters, and an enhancement of the emission intensity can be observed. This interpretation explains several observations. In particular, the observed saturation of the transient enhancement under increasing IR excitation which can be explained as the available shallow trap states being depleted. Further the increasing rise-time observed is likely associated with electrons occupying high-mobility states within the conduction band and reflects the lifetime of the free carrier. The constant fractional enhancement with UV excitation power density shows that at least up to 14 GW/cm^2 we are not yet saturating the empty traps available to receive the photoionized electrons.

Production of traps in MgF_2 by high-energy ionizing radiation or UV excitation has been previously studied.^{7,8} Many of these traps have excited states lying just below the conduction band. For example, the F center excited state is 565 cm^{-1} below the conduction band⁷ and is an efficient intrinsic electron trap. One can estimate the depth of the traps we are observing using the temperature dependence of the signal. It is found that the enhancement effect diminishes in amplitude extremely quickly as the sample temperature

increases above 10 K and is no longer detectable above a temperature of 20 K. This occurs due to thermal escape of electrons and we determine a trap depth of approximately 17 cm^{-1} .

Figure 3 shows the spectral dependence of the transient enhancement. The signal has been integrated over time, and the underlying luminescence from the UV excitation alone subtracted. The spectrum is essentially flat between 400 and 1100 cm^{-1} whilst the apparent drop in signal at higher energies matches very well the FEL power, which reduces at shorter wavelengths for the laser settings used in this experiment. A simple model of a Coulomb or delta trap⁹ with a trap depth of 17 cm^{-1} is consistent with our observed spectral response, since in this experiment the excitation energy is in the essentially flat high-energy tail.

In summary, we have observed trap liberation in $\text{MgF}_2\text{:Yb}^{2+}$ in a two-color excitation experiment that uses infrared pulses to liberate trapped electrons subsequent to excitation of Yb^{2+} at 335 nm. A risetime can be observed on the induced signal which is as long as $21\text{ }\mu\text{s}$ for high infrared excitation densities and the magnitude of the effect appears to saturate. The trap-liberation spectrum is essentially flat over the wavelength range studied and this is consistent with the observed temperature dependence of the effect from which we derive a trap depth of 17 cm^{-1} under the assumption of a Coulomb trap model. This value is quite different from CaF_2 and SrF_2 (Refs. 3 and 4) which have trap depths around 400 cm^{-1} . However MgF_2 has the rutile structure and is, therefore, fundamentally different from both CaF_2 and SrF_2 .

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¹P. Dorenbos, *J. Phys. Condens. Matter* **15**, 575 (2003).

²P. Dorenbos, *J. Phys. Condens. Matter* **15**, 2645 (2003).

³M. F. Reid, P. S. Senanayake, J.-P. R. Wells, G. Berden, A. Meijerink, A. Salkeld, C.-K. Duan, and R. J. Reeves, *Phys. Rev. B* **84**, 113110 (2011).

⁴P. S. Senanayake, J.-P. R. Wells, M. F. Reid, G. Berden, A. Meijerink, and R. J. Reeves, "Impurity-trapped excitons and electron traps in $\text{CaF}_2\text{:Yb}$ and $\text{SrF}_2\text{:Yb}$ probed by transient photoluminescence enhancement," *J. Lumin.* (in press).

⁵M. Forcales, T. Gregorkiewicz, I. V. Bradley, and J.-P. R. Wells, *Phys. Rev. B* **65**, 195208 (2002).

⁶S. Lizzo, A. Meijerink, G. J. Dirksen, and G. Blasse, *J. Lumin.* **63**, 223 (1995).

⁷G. P. Summers, *J. Phys. C: Solid State Phys.* **8**, 3621 (1975).

⁸A. P. Sergeev and P. B. Sergeev, *Quantum Electron.* **38**, 251 (2008).

⁹T. Gregorkiewicz, D. T. X. Thao, and J. M. Langer, *Appl. Phys. Lett.* **75**, 4121 (1999).